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Anmelder/Applicant(s)/Demandeur(s):

BP Lavéra SNC  
Parc Saint-Christophe,  
Bâtiment Newton 1,  
10 avenue de l'Entreprise  
95866 Cergy Pontoise Cedex  
FRANCE

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Supported catalysts

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### SUPPORTED CATALYSTS

The present invention relates to supported catalysts suitable for the polymerisation of olefins and in particular to supported catalysts suitable for the preparation of polymers having broad molecular weight distributions and improved melt strengths.

5        In recent years there have been many advances in the production of polyolefin copolymers due to the introduction of transition metal compounds and in particular metallocene catalysts. Metallocene catalysts offer the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature the polyolefin copolymers  
10       produced by metallocene catalysts often are quite uniform in their molecular structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD) and narrow Short Chain Branching Distribution (SCBD). Although certain properties of metallocene products are enhanced by narrow MWD, difficulties are often encountered in the processing of  
15       these materials into useful articles and films relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain structures to be obtained.

      The use of these metal complex based olefin polymerisation catalysts is now well established. Typically the metallocene complex comprises a bis(cyclopentadienyl)  
20       zirconium complex for example bis(cyclopentadienyl) zirconium dichloride or bis(tetramethylcyclopentadienyl) zirconium dichloride. Examples of such complexes may be found in EP 129368, EP 206794, and EP 260130.

In such catalyst systems the metal complex is used in the presence of a suitable activator. The activators most suitably used with such metallocene complexes are aluminoxanes, most suitably methyl aluminoxane (MAO). Other suitable activators are boron compounds, in particular perfluorinated boron compounds.

5 More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In such complexes the metal atom eg. zirconium or titanium is in the highest oxidation state.

10 Other complexes however have been more recently developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

The above monocyclopentadienyl metallocene complexes are utilised for  
15 polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or compounds based on boron compounds. Examples of the latter are boranes, for example tris(pentafluorophenyl) borane, or borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-borates. Catalyst systems incorporating such borate activators are  
20 described in EP 561479, EP 418044 and EP 551277.

When used for the gas phase polymerisation of olefins, metallocene complexes may typically be supported for example on an inorganic oxide such as silica. Such supports may be typically dehydrated by calcining before use or may be pretreated with an organoaluminium compound to passivate the surface of the silica.

25 Numerous references have described the use of supported metallocene catalyst compositions for use in the gas phase polymerisation of olefins. A number have also described the combination of more than one activator with such supported metallocene complexes.

The aforementioned WO 95/00526 describes in general terms the use of the  
30 reduced oxidation state monocyclopentadienyl complexes with combinations of activators for example aluminoxanes and organoboranes. Although supported catalyst systems are described, all the examples of gas phase polymerisations with supported

catalysts are limited to the use of a single activator, typically tris(pentafluorophenyl) borane.

WO 99/15534 describes the combination of aluminoxanes with a fluoroaryl ligand source such as tris(pentafluorophenyl) borane as activators for metallocene complexes. When supported the activator combinations may be used for the gas phase polymerisation of olefins. The gas phase examples in the reference utilise silica supports that have been calcined prior to contact with the activator components.

WO 00/15672 describes functionalized catalyst supports having chemically bonded aluminium containing groups prepared by the combination of supports having reactive functional groups with a source of aluminium. Where exemplified, in the gas phase, the use of aluminoxane/borane activator combinations are supported on silica which has been dehydrated.

We have now surprisingly found that when supports are pretreated with more than one organoaluminium compound the resultant supported catalysts may be used to prepare polymers having broad molecular weight distributions and improved melt strengths.

Thus according to the present invention there is provided a support material *characterised in that* said support material has been pretreated with at least two different organoaluminum compounds

Preferred support materials for use in the present invention are particulated solid support materials.

The support material may be any organic or inorganic inert solid. However particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins, which have well-known advantages in catalysis, are preferred.. Suitable inorganic oxide materials which may be used include Group 2, 13, 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof.

Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed such as finely divided polyolefins such as polyethylene.

Suitable volume average particle sizes of the support are from 1 to 1000  $\mu\text{m}$  and preferably from 10 to 100  $\mu\text{m}$ .

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica.

Suitable silicas include Crossfield ES70 and Davidson 948 silicas.

5 The support material may be subjected to a heat treatment to reduce the water content or the hydroxyl content of the support material. For example prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure, for example, for 5 hrs.

The support is preferably dehydrated before treatment with the organoaluminium compounds.

10 Most preferably the support material is contacted with the organoaluminium compounds at room temperature in a suitable solvent, for example hexane.

Preferred organoaluminium compounds are trialkyl aluminium compounds containing from 1 to 20 carbons atoms in each alkyl group. Preferred trialkylaluminium compounds are trimethylaluminium, triethylaluminium, triisopropylaluminium and  
15 triisobutylaluminium.

The ratio of aluminium to silica in the pretreated supports of the present invention is such that all the available hydroxy groups are passivated by the pretreatment with the aluminium compounds.

20 In the preferred embodiment of the present invention the support material is pretreated sequentially with the organoaluminium compounds.

The particulated supports of the present invention are suitable for use as a component of a catalyst system suitable for the (co-) polymerisation of olefins. In particular the supports are useful as components of catalyst systems comprising transition metal compounds and activators.

25 Thus according to another aspect of the present invention there is provided a supported catalyst composition prepared by contacting

- (a) a transition metal compound,
- (b) a support, and
- (c) an activator

30 *characterised in that* said support material has been treated sequentially with at least two different organoaluminum compounds

The transition metal compound may be any suitable compound known in the art

R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system,

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\pi$ -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire C<sub>3</sub>R'<sub>4</sub> group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C<sub>1-10</sub> hydrocarbyl.

Most preferred complexes are amidosilane - or amidoalkanedyl complexes.

Most preferred complexes are those wherein M is titanium.

Specific complexes suitable for use in the process according to the present invention are those disclosed in the aforementioned WO 95/00526, the relevant parts of which are incorporated herein by reference.

A particularly preferred complex for use in the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3-pentadiene.

Suitable activators for use with the supports of the present invention include aluminoxanes and organoboron compounds.

Aluminoxanes are well known as activators for metallocene complexes. Suitable aluminoxanes, for use in the process of the present invention, include polymeric or oligomeric aluminoxanes in particular methyl aluminoxane (MAO).

The aluminoxanes suitable for use in the present invention may be commercially

for use as a catalyst component for the polymerisation of olefins.

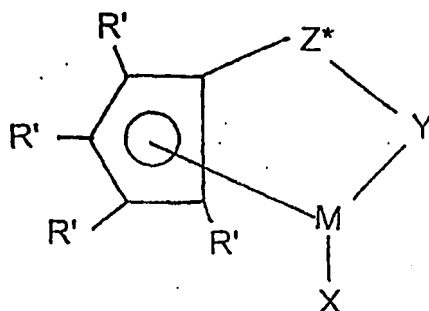
The preferred transition metal compounds are metallocene complexes.

Typically the metallocene complex comprises a bis(cyclopentadienyl) zirconium complex for example bis(cyclopentadienyl) zirconium dichloride or

5 bis(tetramethylcyclopentadienyl) zirconium dichloride. Examples of such complexes may be found in EP 129368, EP 206794, and EP 260130.

Particularly preferred metallocene complexes are monocyclopentadienyl complexes. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436.

10 The preferred monocyclopentadienyl metallocene complexes have the formula



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to  
15 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$  complex with M;

20 Y is -O-, -S-, -NR\*-, -PR\*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ , wherein:



available material or may be such commercially available material that has been dried under vacuum prior to its use for the preparation of the supported catalyst compositions.

Preferred organoboron compounds are triarylboron compounds, in particular perfluorinated triarylboron compounds.

5       The most preferred organoboron compound is tris(pentafluorophenyl) borane (FAB).

Ionic compounds are also suitable for use with the supports of the present invention.

Preferred ionic compounds are those comprising a cation and an anion.

10       The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also  
15       suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic activators used as activators are those wherein the cation of the ionic activator comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate.

Typical borates suitable as ionic activators include:

20       triethylammonium tetraphenylborate  
      triethylammonium tetraphenylborate,  
      tripropylammonium tetraphenylborate,  
      tri(n-butyl)ammonium tetraphenylborate,  
      tri(t-butyl)ammonium tetraphenylborate,  
25       N,N-dimethylanilinium tetraphenylborate,  
      N,N-diethylanilinium tetraphenylborate,  
      trimethylammonium tetrakis(pentafluorophenyl) borate,  
      triethylammonium tetrakis(pentafluorophenyl) borate,  
      tripropylammonium tetrakis(pentafluorophenyl) borate,  
30       tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
      N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,  
      N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

Particularly suitable activators of this type are those ionic activators comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen,

Suitable activators of this preferred type are described in WO 98/27119 the  
5 relevant portions of which are incorporated herein by reference.

Most particularly preferred activators of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred activator is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

10 A particularly preferred supported catalyst system comprises an activator component comprising an organoboron compound and an organoaluminium compound.

Thus according to the present invention there is provided an olefin polymerisation process comprising contacting one or more olefin monomers with a supported catalyst composition prepared by contacting

- 15 (a) a transition metal compound,  
(b) a support, and  
(c) an activator comprising (i) an organoaluminium compound and (ii) an organoboron compound,

characterised in that said support material has been pretreated with at least two  
20 different organoaluminum compounds

The organoaluminium compounds are as described above. The preferred organoaluminium compounds are triethylaluminium or triisobutylaluminium.

The ratio of boron/transition metal in the supported complexes of the present invention is typically in the range 0.1 to 10 and most preferably in the range 1 to 4.

25 The supported catalyst compositions of the present invention may be suitable for use in any polymerisation process for example bulk, slurry or gas phase.

The preferred process is a gas phase process.

The preferred gas phase process takes place continuously in a fluidised bed.

The continuous polymerisation is effected in the gas phase at elevated  
30 temperature in the presence of a fluidised bed of polymer particles and continuous recycle of unreacted monomer(s) around a loop joining the inlet and outlet of the reactor containing the fluidised bed. Examples of two possible approaches are described in EP

89961, US 53527947 and US 5541270 the complete texts of which are herein incorporated by reference. EP 699213 also illustrates a possible approach and again the complete text of this publication is incorporated by reference.

The process of the present invention is suitable for the polymerisation of  
5 ethylene or the copolymerisation of ethylene with one or more alpha-olefins having from three to twenty carbon atoms. Preferably the alpha-olefin has between three and ten carbon atoms most preferably three and eight. Examples of the most preferred alpha olefins include 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene.

The process of the present invention is most particularly directed to the  
10 preparation of copolymers of ethylene with alpha-olefins having at least 6 carbon atoms in particular to copolymers of ethylene with 1-hexene or 4-methyl-1-pentene.

It has been surprisingly found that the supported catalyst systems described herein may be used to prepare copolymers having a broad molecular weight distribution as well as improved melt strengths.

15 Copolymers may be prepared which exhibit a molecular weight distribution (Mw/Mn) of  $> 2$ .

The copolymers also exhibit melt strength values in the range 3 – 12 cN and preferably in the range 3 – 9 cN.

The copolymers are preferably prepared by use of a supported metallocene  
20 catalyst system as hereinbefore described.

Thus according to another aspect of the present invention there is provided a process for the preparation of copolymers of ethylene and alpha-olefins having

(a) melt strength in the range 3 – 12 cN,

(b) a Mw/Mn of  $> 2$ .

25 said process comprising contacting ethylene and one or more alpha-olefins in the presence of a supported catalyst system as hereinbefore described.

The preferred supported catalyst system for this aspect of the present invention is that wherein the transition metal compound is a monocyclopentadienyl metallocene complex as hereinbefore described.

30 The preferred process for the preparation of such copolymers is a gas phase process.

The process of the present invention will now be illustrated by reference to the

following examples.

Examples

Abbreviations used

FAB trispentafluorophenylborane  $B(C_6F_5)_3$

5 TEA triethylaluminium

TiBA trisobutylaluminium

Complex A (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl  
silanetitanium - $\eta^4$ -1,3-pentadiene

10 All catalyst preparation steps were performed in a inert atmosphere filled glove-  
box using standard Schlenk and cannulae techniques.

Example 1

To 5 g of Ineos ES70 silica (previously calcined at 500°C for 5 hours under  
nitrogen, pore volume 1.55 ml/g) was added 2.04 ml of an hexane solution of  
triethylaluminium (TEA), 0.98 mol/l, (0.4 mmol Al/ g silica) followed by the addition  
15 of 1.58 ml of an hexane solution of TiBA, 0.95 mol/l (0.3 mmol Al/g silica). The  
mixture was allowed to react for 2 hours then dried under vacuum.

To 0.77 g of trispentafluorophenylborane (1.5 mmol) was added 5 ml of toluene.  
1.53 ml of a solution of triethylaluminum in hexane, 1 mol/l, were then added and the  
solution was stirred for 30 minutes.

20 The trispentafluorophenylalane above was added to the TEA-TiBA treated silica  
(at pore volume) and then heated at 85°C for 2 hours, followed by drying at the same  
temperature

1.4 ml of Complex A solution in heptane (9.17 % wt) was then slowly added (15  
min) and manually agitated until no lumps were visible.

25 One hour holding

Catalyst was then dried under vacuum

[Ti] = 66  $\mu$ mol/g final catalyst; [Al]= 0.908 mmol/g final catalyst

Polymerisation data

Run conditions :

30 200 g of PE pellets as bed

T = 70°C

PC2= 6.5 Bar.

PC6/PC2 = 0.0048

SiO2/TEA impregnated used as scavenger.

H2 added during the gas phase composition: 150 ml

Catalyst quantity: 200 mg

5 Polymerisation time = 60min

At the end of the polymerisation reaction, polymer produced separated from polymer bed by simple sieving was obtained having the following properties:

	Activity:	24 g/ghb
	MI (2.16 kg)	0.81 g/10 min
10	Density	0.926 g/ml
	Mn	19300 g/mol
	Mw	114125 g/mol
	Mw/Mn	5.9
	Melt strength(16 Mpa)	7.6 (cN)

15 Product characteristics were determined using the following analytical procedures:

Melt Flow Rate (2.16 kg)

The melt flow rate (MFR) of the polymers was measured under conditions which conform to ISO 1133 (1991) and BS 2782:PART 720A:1979 procedures. The weight of polymer extruded through a die of 2.095 mm diameter, at a temperature of 190°C, during a 600 second time period and under a standard load of 2.16 kg is recorded.

Molecular Structure Characterisation

25 Various techniques (eg  $^{13}\text{C}$  NMR, GPC/LALLS, GPC/intrinsic viscosity, GPC/on-line viscometry and rheological flow activation energy, etc) have been developed to indicate the presence of long chain branching in polymers.

Molecular Weight Distribution ( $M_w/M_n$ )

30 Molecular weight distribution and associated averages, were determined by Gel Permeation Chromatography using a Waters GPCV 2000. The Millennium version 3.05.01 software supplied by Waters was used for data treatment. The solvent used was 1,2,4 Trichlorobenzene at 150°C, stabilised with 0.05% BHT. The nominal flow rate was 1 ml/min. Solutions of concentration around 0.1%w/w were prepared at 150°C for 2

hours on a hot plate, and the nominal injection volume was set at 217.5 ml. 2 Shodex AT806M/S and 1 Waters HT2 columns were used with a plate count (at half height) of typically 28,000. The system was calibrated using 12 polystyrene standards supplied by Polymer Laboratories.

- 5 Apparent molecular weight distribution and associated averages, uncorrected for long chain branching, were determined using the differential refractometer detector alone. Molecular weight of Ps standards were converted to polyethylene molecular weights using the Mark Houwink parameters  $K_{ps} = 1.75 \times 10^{-4} \text{ dl/g}$ ,  $\square_{ps} = 0.67$ ,

$$K_{pe} = 4.1 \times 10^{-4} \text{ dl/g}, \square_{pe} = 0.706 \text{ [Polymer Handbook, J. Bandrup and E.H.}$$

- 10 Immergut, 3<sup>rd</sup> Edition].

This calibration has been checked against the NIST certified polyethylene SRM1475, the values obtained being 54,100 g/mol for  $M_w$  and 17,300 g/mol for  $M_n$ .

#### Melt Strength

- The melt strength of the polymer is measured at 190°C, using a Göttfert
- 15 Rheotens extensional rheometer in conjunction with a Rosand RH 7 Capillary Rheometer. This is achieved by extruding the polymer at a constant pressure (P) through a die of 1.5 mm diameter and 30 mm in length, with a 90° entry angle. Once a given extrusion pressure is selected, the piston of the capillary rheometer will travel through its 15 mm diameter barrel at a speed that is sufficient to maintain that pressure
- 20 constant. The nominal wall shear rate ( $\dot{\gamma}$ ) for a given extrusion pressure can then be computed for the polymer at the selected pressure using the constant pressure ratio system of the rheometer.

- The extrudate is drawn with a pair of gear wheels at an accelerating speed (V). The acceleration ranges from 0.12 to 1.2 cm/s<sup>2</sup> depending on the flow properties of the
- 25 polymer under test. The drawing force (F) experienced by the extrudate is measured with a transducer and recorded on a chart recorder together with the drawing speed. The maximum force at break is defined as melt strength (MS) at a constant extrusion pressure (P) or at its corresponding extrusion rate ( $\dot{\gamma}$ ). Three or four extrusion pressures (6, 8, 12, 16 MPa) are typically selected for each polymer depending on its
- 30 flow properties. For each extrusion pressure, a minimum of 3 MS measurements is performed and an average MS value is then obtained.

The derivative function of the extrusion pressure dependent melt strength;

$\delta(MS)/\delta(P)$  for each polymer is computed from the slope (by a least square line fitting) of the plot of the average MS against pressure. The mean melt strength at an extrusion pressure of 16 MPa,  $MS(16 \text{ MPa})$ , can be computed from the plot.

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Claims

1. A catalyst support material characterised in that said support material has been treated sequentially with at least two different organoaluminium compounds.

2. A supported catalyst composition prepared by contacting

(a) a transition metal compound,

5 (b) a support, and

(c) an activator

characterised in that the support has pretreated with at least two different organoaluminium compounds.

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**ABSTRACT**  
**SUPPORTED CATALYSTS**

A catalyst support material is characterised in having been pretreated with at least two different organaluminium compounds. The supports may be used as components of olefin polymerisation catalyst systems comprising transition metal compounds and activators.

By use of the supported catalyst systems, polymers may be prepared, particularly in the gas phase, having broad molecular weight distributions and improved melt strengths.